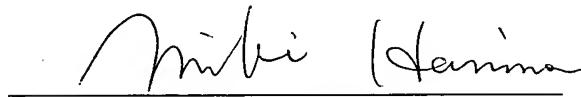


VERIFICATION OF TRANSLATION

Re : Japanese Patent Application No. 2002-382309

I, Miki HARIMA, of c/o Hosoda International Patent Office, OMM Building 5th Floor, P.O. Box 26, 1-7-31 Otemae, Chuo-ku, Osaka 540-6591, JAPAN, hereby declare that I am the translator of the documents attached and certify that the following is a true translation of the best of my knowledge and belief.

Dated this 13th day of January, 2006



Miki HARIMA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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[List of Annexed Documents]

[Document]	Specification	1
[Document]	Abstract	1

[Number of General Authorization] 0012367

[Requirement of Proof] Required

[Document] Specification

[Title of the Invention] Water-Based Ink

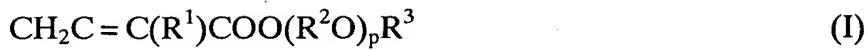
[Claims]

[Claim 1] A water-based ink comprising a water-insoluble polymer having an ionic group at its end and a pigment.

[Claim 2] The water-based ink according to claim 1, wherein the ionic group is an ionic group derived from at least one member selected from the group consisting of a chain transfer agent having an ionic group, a polymerization initiator having an ionic group, and an iniferter having an ionic group and the functions of the chain transfer agent and the polymerization initiator.

[Claim 3] The water-based ink according to claim 1 or 2, wherein the water-insoluble polymer having an ionic group at its end is a water-insoluble vinyl polymer prepared by copolymerizing a monomer mixture comprising (A) a salt-forming group-containing monomer, (B) a macromer, and (C) a monomer copolymerizable with the salt-forming group-containing monomer and the macromer, in the presence of at least one member selected from the group consisting of a chain transfer agent having an ionic group, a polymerization initiator having an ionic group, and an iniferter having an ionic group and the functions of the chain transfer agent and the polymerization initiator.

[Claim 4] The water-based ink according to claim 3, wherein the monomer mixture further comprises at least one monomer selected from the group consisting of (D) a hydroxyl group-containing monomer, and (E) a monomer represented by the formula (I):



wherein R¹ is a hydrogen atom or a lower alkyl group having 1 to 5 carbon atoms; R² is a divalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom; R³ is a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms which may have a hetero atom; and p is a number of 1 to 60, and
wherein (C) the monomer copolymerizable with the salt-forming group-containing monomer and the macromer is a monomer copolymerizable with (D) the hydroxyl group-containing monomer and the monomer of (E).

[Claim 5] The water-based ink according to any one of claims 2 to 4, wherein the chain transfer agent having an ionic group is at least one member selected from the group consisting of thioglycollic acid, mercaptopropionic acid and mercaptosuccinic acid.

[Claim 6] The water-based ink according to any one of claims 1 to 5, wherein the water-based ink comprises an aqueous dispersion of polymer particles of pigment-containing water-insoluble polymer having an ionic group at its end.

[Claim 7] A process for preparing a water-based ink, comprising dissolving a water-insoluble polymer having an ionic group at its end in an organic solvent; adding a pigment, water and a neutralizing agent, and optionally a surfactant to the resulting solution; kneading the mixture to form a paste; diluting the paste with water as occasion demands; and distilling off the organic solvent to make it into a water-based system.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a water-based ink. More specifically, the present invention relates to a water-based ink which can be suitably used for printers for inkjet printing, and a process for preparing the water-based ink.

[0002]

[Prior Art]

As a coloring material for water-based inks for inkjet printers, a water-soluble dye has been widely used because the water-soluble dye is suitable for photographic printing in terms of having a wide range of color tones and being excellent in color reproducibility. However, there are some disadvantages in a water-soluble dye, such that the water-soluble dye has deteriorated water resistance, high-lighter fastness and rubbing resistance.

[0003]

As an ink having improved water resistance, high-lighter fastness and rubbing resistance, there have been proposed water-based inks to which fine polymer particles are added (see, for instance, Patent Publications 1 and 2). However, while it is desired that the water-based inks are improved to a certain extent in water resistance, rubbing resistance and blotting resistance, there are some disadvantages in these water-based inks such that jetting property when jetted with an inkjet printer is insufficient, so that the printouts are likely to become blurry.

[0004]

[Patent Publication 1]

Japanese Patent Laid-Open No. Hei 03-056573

[Patent Publication 2]

Japanese Patent Laid-Open No. Hei 03-160069

[0005]

[Problems to Be Solved by the Invention]

An object of the present invention is to provide a water-based ink which is excellent in water-resistance, high-lighter fastness and rubbing resistance. A further object of the present invention is to provide a water-based ink which is excellent in jetting property when printed with an inkjet printer.

[0006]

[Means to Solve the Problems]

According to the present invention, there are provided:

- (1) a water-based ink comprising a water-insoluble polymer having an ionic group at its end and a pigment; and
- (2) a process for preparing a water-based ink, comprising dissolving particles of water-insoluble polymer having an ionic group at its end in an organic solvent; adding a pigment, water and a neutralizing agent, and optionally a surfactant to the resulting solution; kneading the mixture to form a paste; diluting the paste with water as occasion demands; and distilling off the organic solvent to make it into a water-based system.

[0007]

[Modes for Carrying out the Invention]

The water-based ink of the present invention is excellent in not only pigment dispersion stability, but also jetting property when printed with an inkjet printer, and also shows excellent water resistance, excellent high-lighter fastness and excellent rubbing resistance, since the water-insoluble polymer having an

ionic group at its end is used together with the pigment.

[0008]

The pigment may be any of an inorganic pigment and an organic pigment. The pigment may be used together with an extender as occasion demands.

[0009]

The inorganic pigment includes, for instance, carbon black, metal oxides, metal sulfides and the like. These inorganic pigments can be used alone or in admixture of at least two kinds. The carbon black includes furnace black, thermal lamp black, acetylene black, channel black, gas black and the like.

[0010]

The organic pigment includes, for instance, azo pigments, diazo pigments, phthalocyanine pigments, quinacridone pigments, isoindolinone pigments, dioxazine pigments, perylene pigments, perinone pigments, thioindigo pigments, anthraquinone pigments, quinophthalone pigments and the like. These organic pigments can be used alone or in admixture of at least two kinds.

[0011]

In order to disperse the pigment in the water-based ink as stable fine particles, there can be used a surfactant, a water-soluble polymer or a water-insoluble polymer. Especially, in order to obtain a water-based ink excellent in water resistance, high-lighter fastness and rubbing resistance, it is preferable that the pigment is contained in polymer particles of the water-insoluble polymer.

[0012]

The surfactant used in the dispersion of the pigment includes anionic

surfactants, cationic surfactants, nonionic surfactants or amphoteric surfactants. Among them, a sodium salt of β -naphthalenesulfonate-formaldehyde condensate (for instance, products commercially available from Kao Corporation under the trade names of Demol N, Demol RN, Demol MS and the like), and carboxylate polymer surfactants (for instance, a product commercially available from Kao Corporation under the trade names of Poise 520, Poise 521, Poise 530 and the like) are preferable from the viewpoints of dispersion stability and jetting property.

[0013]

It is desired that the amount of the surfactant is 1 to 120 parts by weight, preferably 3 to 70 parts by weight, more preferably 5 to 30 parts by weight of the surfactant, based on 100 parts by weight of the pigment, from the viewpoints of dispersion stability of the coloring material in the ink and jetting property of the ink.

[0014]

The water-soluble polymer which may be used when the pigment is dispersed in water includes water-soluble vinyl polymers, water-soluble ester polymers, water-soluble urethane polymers and the like. Among these polymers, the water-soluble vinyl polymers are preferable.

[0015]

The term "end" of the water-insoluble polymer as referred to herein means an end of the main chain of the water-insoluble polymer, not an end of the side chain of the water-insoluble polymer. However, when the water-insoluble polymer is a grafted copolymer, the term "end" of the water-insoluble polymer can include an end of a grafted chain.

[0016]

The end of the water-insoluble polymer may be an end derived from a polymerization initiator, an end derived from a chain transfer agent, or an end derived from a monomer.

[0017]

The term "ionic group" as referred to herein means both a functional group already having an electric charge and being in an ionic state, and a functional group not having an electric charge but being capable of forming an ion by external action.

[0018]

The ionic group includes cationic groups, anionic groups and betaine groups. It is preferable that the ionic group exists on one end or both ends of the polymer. The number of the ionic groups per one end is preferably at least one, more preferably at least two, from the viewpoint of hydrophilicity.

[0019],

Concrete examples of the cationic group include an amine base represented by the formula: $-\text{NH}_n\text{R}^{4-}_{2-n}$, wherein n is an integer of 0 to 2, each R^4 is independently an alkyl group or aryl group; pyridinium salt; imidazolium salt; a phosphine group represented by the formula: $-\text{P}(\text{R}^5)_2$, wherein each R^5 is independently an alkyl or aryl group; and the like. Each of these cationic groups may be used alone or in admixture of at least two kinds. Among them, the amine base is preferable from the viewpoints of dispersion stability of an ink and satisfaction of water resistance and rubbing resistance. The above-mentioned alkyl group is preferably an alkyl group having 1 to 8 carbon atoms, and the above-mentioned aryl group is preferably an aryl group having 6

to 12 carbon atoms.

[0020]

Concrete examples of the anionic group include $-COOM$ group, wherein M is a hydrogen atom or an alkali metal atom, hereinafter referred to the same, $-SO_3M$ group, $-PO_3M_2$ group and the like. Each of these anionic groups may be used alone or in admixture of at least two kinds.

[0021]

Concrete examples of the betaine-based group include carbobetaine group, sulfobetaine group, phosphobetaine group, for instance, those compounds having amino group and carboxyl group in its molecule, such as amino acids. These betaine-based groups can be used alone or in admixture of at least two kinds. Among them, the compound having amino group and carboxyl group in its molecule is preferable from the viewpoints of dispersion stability of an ink and satisfaction of water resistance and rubbing resistance.

[0022]

It is preferable that the ionic group is an ionic group derived from at least one member selected from the group consisting of a chain transfer agent having an ionic group, a polymerization initiator having an ionic group and an iniferter having an ionic group which has the functions of the chain transfer agent and the polymerization initiator (hereinafter simply referred to as "iniferter").

[0023]

The water-insoluble polymer having an ionic group at its end can be obtained by polymerizing monomers in the presence of at least one member selected from the group consisting of the chain transfer agent having an ionic group, the polymerization initiator having an ionic group and the iniferter.

[0024]

The polymerization initiator having an ionic group includes

2,2'-azobis(2-amidinopropane), dibasic acids, 4,4'-azobis(4-cyanovaleric acid),
2,2'-azobis[2-(5-methyl-2-imidazolin-2-yl)propane] dihydrochloride,
2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride,
2,2'-azobis[2-(2-imidazolin-2-yl)propane] disulfate dihydrate,
2,2'-azobis[2-(3,4,5,6-tetrahydropyrimidin-2-yl)propane] dihydrochloride,
2,2'-azobis[2-(1-(2-hydroxyethyl)-2-yl)propane] dihydrochloride and the like.

[0025]

The chain transfer agent having an ionic group may be those having a functional group for causing chain transfer and an ionic group. The functional group for causing chain transfer includes, for instance, mercapto group, disulfide group and the like. Among them, mercapto group is preferable. There is no limitation in the number of ionic groups in the chain transfer agent having an ionic group, and the number of ionic groups may be at least 2.

[0026]

Concrete examples of the chain transfer agent having an ionic group includes chain transfer agents having cationic group, such as 1-amino-2-methyl-2-propanethiol, 2-aminoethanethiol, 2-diethylaminoethanethiol, 2-dimethylaminoethanethiol, 4-aminothiophenol, dithiodianiline, 3,4,5,6-tetrahydro-2-pyrimidinethiol and 2-mercaptopthiazoline; chain transfer agents having anionic group, such as thioglycollic acid, mercaptopropionic acid, mercaptosuccinic acid, thiolactic acid, 4,4'-dithiobutyric acid, 3,3'-dithiopropionic acid and dithioglycollic acid; and chain transfer agents having betaine-based group, such as thiol group-containing amino acids such as

DL-penicillamine, N-(2-mercaptopropionyl)glycine, DL-cysteine, DL-homocysteine, cystamine, DL-cystine and their derivatives. These chain transfer agents can be used alone or in admixture of at least two kinds.

[0027]

From the viewpoint of obtaining a water-based ink being excellent in jetting property, 2-aminoethanethiol and 2-diethylaminoethanethiol are preferable among the chain transfer agents having a cationic group; thioglycollic acid, mercaptosuccinic acid and mercaptopropionic acid are preferable among the chain transfer agents having an anionic group; and DL-cysteine is preferable among the chain transfer agents having a betaine-based group. Among them, thioglycollic acid, mercaptopropionic acid and mercaptosuccinic acid are more preferable, and mercaptosuccinic acid which is a chain transfer agent having two ionic groups at one end is still more preferable.

[0028]

When the chain transfer agent not having an electric charge but being capable of forming an ion by external action is used, all or a part of the functional groups are ionized before the preparation of the water-based ink. The ionization of the functional group can be carried out by adding an ionizing compound to this chain transfer agent, thereby ionizing the functional group of the chain transfer agent, or ionizing the functional group in its molecule by the functional group which is present in the water-insoluble polymer.

[0029]

For instance, when the monomers are polymerized in the presence of thioglycollic acid as a chain transfer agent, an alkaline compound capable of neutralizing an active hydrogen of thioglycollic acid may be added to the

resulting polymerization reaction mixture. The alkaline compound includes, for instance, sodium hydroxide, potassium hydroxide, aqueous ammonia and the like. However, even in this case, when the monomer having amino group is contained in the monomers constituting the polymer, since end carboxyl group of the produced polymer has been already ionized, addition of the alkaline compound would not be necessitated at the termination of the polymerization.

[0030]

When the chain transfer agent having a cationic group is used as a chain transfer agent, there can be used a compound having an opposite electric charge, namely a compound having an anionic property.

[0031]

It is preferable that the amount of the chain transfer agent having an ionic group is 0.001 to 10 parts by weight based on 100 parts by weight of the entire monomers provided in the polymerization from the viewpoint of obtaining a water-based ink being excellent in jetting property and from the viewpoint of improving dispersion stability of the water-insoluble polymer. Also, the amount of the chain transfer agent having an ionic group is preferably 0.01 to 7 parts by weight, more preferably 0.1 to 5 parts by weight, based on 100 parts by weight of the entire monomers provided in the polymerization from the viewpoints of obtaining a water-based ink being excellent in water resistance, rubbing resistance, jetting property and blotting resistance.

[0032]

The term "water-insoluble" used in the water-insoluble polymer as referred to herein means that the amount of the polymer dissolved in 100 g of water at 25°C is less than 2 g when the salt-forming group of the polymer is

neutralized at the time of dissolving the polymer in an organic solvent and preparing an aqueous dispersion of the polymer, and thereafter the aqueous dispersion is dried at 105°C for 2 hours to give a polymer. The term "water-soluble" means those other than that defined as "water-insoluble."

[0033]

The iniferter includes 1,2-biscarboxymethyl-1,1,2,2-tetraphenylethane, 1,2-bis(2-carboxyethyl)-1,1,2,2-tetraphenylethane and the like.

[0034]

Among the chain transfer agent having an ionic group, the polymerization initiator having an ionic group and the iniferter, the chain transfer agent having an ionic group is preferable because the compound can be conveniently used.

[0035]

Kinds of the monomers constituting the polymer in the present invention are not limited to specified ones. It is preferable that the water-insoluble polymer is a water-insoluble vinyl polymer in order to maximally exhibit excellent jetting property, water resistance, high-lighter fastness and rubbing resistance. It is more preferable that the water-insoluble vinyl polymer is a water-insoluble vinyl polymer prepared by copolymerizing a monomer mixture comprising (A) a salt-forming group-containing monomer [hereinafter referred to as component (A)], (B) a macromer [hereinafter referred to as component (B)], and (C) a monomer copolymerizable with the salt-forming group-containing monomer and the macromer [hereinafter referred to as component (C)], in the presence of at least one member selected from the group consisting of a chain transfer agent having an ionic group, a polymerization initiator having an ionic

group and the above-mentioned iniferter.

[0036]

The component (A) includes a cationic monomer, an anionic monomer and the like. Examples of the component (A) include the cationic monomers and the anionic monomers described at page 5, column 7, line 24 to column 8, line 29 of Japanese Patent Laid-Open No. Hei 9-286939.

[0037]

Representative examples of the cationic monomer include unsaturated monomers having an amine group, unsaturated monomers having an ammonium salt group and the like. Among them, N,N-dimethylaminoethyl (meth)acrylate, N-(N',N'-dimethylaminopropyl) (meth)acrylamide and vinylpyrrolidone are preferable.

[0038]

Representative examples of the anionic monomer include unsaturated carboxylic acid monomers, unsaturated sulfonic acid monomers, unsaturated phosphoric acid monomers and the like. Among them, the unsaturated carboxylic acid monomers such as acrylic acid and methacrylic acid are preferable.

[0039]

The content of the component (A) in the water-insoluble vinyl polymer is preferably 1 to 50% by weight, more preferably 2 to 40% by weight from the viewpoint of dispersion stability of the resulting dispersion.

[0040]

The component (B) includes a macromer having a polymerizable unsaturated group and a number-average molecular weight of 500 to 100000,

preferably 1000 to 10000. Among them, a styrenic macromer having a polymerizable functional group at one end is preferable because of its high affinity for the colorant.

[0041]

The number-average molecular weight of the component (B) is determined by gel permeation chromatography using chloroform containing 1 mmol/L dodecyldimethylamine as a solvent, with polystyrene as a standard substance.

[0042]

The content of the component (B) in the water-insoluble vinyl polymer is preferably 1 to 25% by weight, more preferably 5 to 20% by weight especially from the viewpoint of improving dispersion stability of pigment-containing polymer particles.

[0043]

The styrenic macromer includes a styrene homopolymer having a polymerizable functional group at one end or a copolymer of styrene and other monomer, having a polymerizable functional group at one end. Among them, those having acryloyl group or methacryloyl group at one end as a polymerizable functional group are preferable. The content of styrene in the macromer is preferably at least 50% by weight, more preferably at least 70% by weight from the viewpoint of improving affinity for a pigment. The other monomer includes acrylonitrile and the like.

[0044]

The component (C) includes, for instance, (meth)acrylates having an ester moiety of 1 to 30 carbon atoms, such as methyl (meth)acrylate, ethyl

(meth)acrylate, (iso)propyl (meth)acrylate, (iso or tertiary)butyl (meth)acrylate, (iso)amyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, (iso)octyl (meth)acrylate, (iso)decyl (meth)acrylate, (iso)dodecyl (meth)acrylate and (iso)stearyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, 2-methylstyrene and chlorostyrene; and the like. These monomers can be used alone or in admixture of at least two kinds.

[0045]

Incidentally, the terms "(iso- or tertiary-)" and "(iso)" as referred to herein include both cases where these groups are present and where they are absent. In the case where these groups are absent, each of the listed compounds has a normal form. Also, "(meth)acrylate" means acrylate or methacrylate.

[0046]

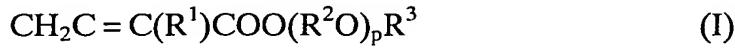
It is preferable that the component (C) contains a styrenic monomer from the viewpoint of improving optical density and high-lighter fastness of the water-based ink. As the styrenic monomer, styrene and 2-methylstyrene are preferable. These styrenic monomers may be used alone or in admixture of at least two kinds. In this case, the content of the styrenic monomer in the component (C) is preferably 10 to 100% by weight, more preferably 40 to 100% by weight from the viewpoint of improving optical density and high-lighter fastness of the water-based ink.

[0047]

The content of the component (C) in the water-insoluble vinyl polymer is preferably 5 to 88% by weight, more preferably 10 to 60% by weight from the viewpoint of improving water resistance, rubbing resistance and high-lighter fastness of the water-based ink.

[0048]

In addition, the monomer mixture may contain at least one monomer selected from the group consisting of (D) a hydroxyl group-containing monomer [hereinafter referred to as component (D)], and (E) a monomer represented by the formula (I):



wherein R^1 is a hydrogen atom or a lower alkyl group having 1 to 5 carbon atoms; R^2 is a divalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom; R^3 is a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom; and p is a number of 1 to 60.

[0049]

The component (D) exhibits some excellent effects such as increase of dispersion stability and improvement of high-lighter fastness in a short period of time during printing.

[0050]

The component (D) includes, for instance, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, polyethylene glycol($n=2$ to 30, wherein n is the number of moles of ethylene oxide added, hereinafter referred to the same) (meth)acrylate, poly(ethylene glycol($n=1$ to 15)-propylene glycol($n=1$ to 15)) (meth)acrylate and the like. Among them, 2-hydroxyethyl (meth)acrylate is preferable.

[0051]

The content of the component (D) in the water-insoluble vinyl polymer is preferably 5 to 40% by weight, more preferably 7 to 20% by weight from the viewpoint of improving jetting stability, optical density and high-lighter fastness of the water-based ink.

[0052]

The total content of the component (A) and the component (D) in the water-insoluble vinyl polymer is preferably 6 to 60% by weight, more preferably 10 to 50% by weight, from the viewpoint of improving stability of the water-insoluble polymer in water and water resistance of the water-based ink.

[0053]

The component (E) exhibits some excellent effects such as further increase of jetting stability of a water-based ink, and suppression of the generation of crookedness even in continuous printing.

[0054]

In the formula (I), R¹ is a hydrogen atom or a lower alkyl group having 1 to 5 carbon atoms. Among them, hydrogen atom and methyl group are preferable.

[0055]

R² is a divalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom. The hetero atom includes, for instance, nitrogen atom, oxygen atom, a halogen atom and sulfur atom.

[0056]

Representative examples of R² include an aromatic ring having 6 to 30 carbon atoms which optionally has a substituent; a heterocyclic ring having 3 to 30 carbon atoms which optionally has a substituent; and an alkylene group

having 1 to 30 carbon atoms which optionally has a substituent. These rings or groups may be used in combination of at least two kinds. The substituent includes an aromatic ring having 6 to 29 carbon atoms, a heterocyclic ring having 3 to 29 carbon atoms, an alkyl group having 1 to 29 carbon atoms, halogen atoms, amino group and the like.

[0057]

Preferred examples of R^2 include a phenylene group which optionally has a substituent of 1 to 24 carbon atoms; an aliphatic alkylene group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms; an aromatic ring-containing alkylene group having 7 to 30 carbon atoms; and a heterocyclic ring-containing alkylene group having 4 to 30 carbon atoms.

[0058]

Preferred examples of the R^2O group include an oxyalkylene group having 2 to 7 carbon atoms, such as oxyethylene group, oxy(iso)propylene group, oxytetramethylene group, oxyheptamethylene group, oxyhexamethylene group and a combination of at least one member of these oxyalkylenes; and oxyphenylene group.

[0059]

R^3 is a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom. The hetero atom includes, for instance, nitrogen atom, oxygen atom and sulfur atom.

[0060]

Representative examples of R^3 include an aromatic ring having 6 to 30 carbon atoms which optionally has a substituent; a heterocyclic ring having 3 to 30 carbon atoms which optionally has a substituent; or an alkyl group having 1 to

30 carbon atoms which optionally has a substituent. The substituent includes an aromatic ring having 6 to 29 carbon atoms, a heterocyclic ring having 4 to 29 carbon atoms, halogen atoms, amino group and the like.

[0061]

Preferred examples of R³ include phenyl group, an aliphatic alkyl group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, an aromatic ring-containing alkyl group having 7 to 30 carbon atoms, and a heterocyclic ring-containing alkyl group having 4 to 30 carbon atoms.

[0062]

More preferable examples of R³ include alkyl groups having 1 to 6 carbon atoms, such as methyl group, ethyl group, (iso)propyl group, (iso)butyl group, (iso)pentyl group and (iso)hexyl group, and phenyl group.

t[sic] is a number of 1 to 60, especially preferably a number of 1 to 30.

[0063]

Concrete examples of the component (E) include methoxypolyethylene glycol (1-30: showing the value of p in the formula (I), hereinafter referred to the same) (meth)acrylates, methoxypolytetramethylene glycol (1-30) (meth)acrylates, ethoxypolyethylene glycol (1-30) (meth)acrylates, (iso)propoxypolyethylene glycol (1-30) (meth)acrylates, butoxypolyethylene glycol (1-30) (meth)acrylates, methoxypolypropylene glycol (1-30) (meth)acrylates, methoxy(ethylene glycol-propylene glycol copolymer) (1-30, out of which ethylene glycol: 1-29) (meth)acrylates and the like. These monomers can be used alone or in admixture of at least two kinds. Among them, the methoxypolyethylene glycol (1-30) (meth)acrylates are preferable.

[0064]

The content of the component (E) in the water-insoluble vinyl polymer is 5 to 50% by weight, preferably 10 to 40% by weight, from the viewpoint of improving jetting stability of the water-based ink and dispersion stability of the water-insoluble polymer.

[0065]

Also, the total content of the component (A) and the component (E) in the water-insoluble vinyl polymer is preferably 6 to 75% by weight, more preferably 13 to 50% by weight from the viewpoint of improving dispersion stability of the water insoluble polymer in water and jetting stability of the water-based ink.

[0066]

The total content of the component (A), the component (D) and the component (E) in the water-insoluble vinyl polymer is preferably 11 to 60% by weight, more preferably 19 to 50% by weight from the viewpoint of improving dispersion stability of the water insoluble polymer in water and jetting stability of the water-based ink.

[0067]

The water-insoluble vinyl polymer can be prepared by copolymerizing a monomer mixture by a known polymerization method such as a bulk polymerization method, a solution polymerization method, a suspension polymerization method or an emulsion polymerization method. Among these polymerization methods, the solution polymerization method is preferable.

[0068]

The solvent used in the solution polymerization method is not limited to specified ones, and a polar organic solvent is preferable. The polar organic

solvent can be used in admixture with water.

[0069]

The polar organic solvent includes, for instance, aliphatic alcohols having 1 to 3 carbon atoms, such as methanol, ethanol and propanol; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters such as ethyl acetate; and the like. Among them, ethanol, acetone, methyl ethyl ketone, methyl isobutyl ketone or a liquid mixture of the solvent and water is preferable.

[0070]

A radical polymerization initiator can be used in the polymerization. As the radical polymerization initiators, preferable are azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), dimethyl-2,2'-azobisbutyrate, 2,2'-azobis(2-methylbutyronitrile) and 1,1'-azobis(1-cyclohexanecarbonitrile). Also, as radical polymerization initiators, there can be used organic peroxides such as t-butyl peroxyoctoate, di-t-butyl peroxide and dibenzoyl oxide.

[0071]

The amount of the radical polymerization initiator is preferably 0.001 to 5% by weight, more preferably 0.01 to 2% by weight in the monomer mixture.

[0072]

The conditions for polymerizing the monomer mixture differ depending upon kinds of the radical polymerization initiator, monomers and solvent used, and the like. Usually, the polymerization temperature is 30° to 100°C, preferably 50° to 80°C, and the polymerization time is 1 to 20 hours. It is preferable that the atmosphere for polymerization is an atmosphere of an inert gas such as nitrogen gas.

[0073]

After termination of the polymerization reaction, the water-insoluble vinyl polymer can be isolated from the reaction solution by a known method such as re-precipitation or solvent distillation. Also, the resulting water-insoluble vinyl polymer can be purified by removing unreacted monomers and the like therefrom by repeat of re-precipitation, membrane separation, a chromatographic method, an extraction method or the like.

[0074]

It is preferable that the weight-average molecular weight of the water-insoluble vinyl polymer is 3000 to 100000, as determined in accordance with the method described in Examples, from the viewpoints of water resistance, rubbing resistance, high-lighter fastness and dispersion stability after printing.

[0075]

As the neutralizing agent for the water-insoluble vinyl polymer, an acid or a base can be used in accordance with the kind of the salt-forming group of the polymer. The acid includes inorganic acids such as hydrochloric acid and sulfuric acid; and organic acids such as acetic acid, propionic acid, lactic acid, succinic acid, glycollic acid, gluconic acid and glyceric acid. The base includes amines such as trimethylamine, triethylamine, diethanolamine, N-methyldiethanolamine and triethanolamine; ammonia; alkali metal hydroxides such as sodium hydroxide and potassium hydroxide; and the like.

[0076]

The neutralization degree of the water-insoluble vinyl polymer is not limited to specified ones. It is preferable that the resulting aqueous dispersion is usually neutral, for instance the pH of the aqueous dispersion is 4.5 to 9.5.

[0077]

After the neutralization of the water-insoluble vinyl polymer, the water-insoluble vinyl polymer can be solely contained in the ink. Alternatively, polymer particles of the water-insoluble vinyl polymer containing a colorant can be contained in the ink. Among them, the polymer particles of the water-insoluble vinyl polymer containing a colorant are preferable from the viewpoint of satisfying all of water resistance, high-lighter fastness, rubbing resistance, jetting property and blotting resistance.

[0078]

The amount of the water-insoluble polymer in the ink is 0.05 to 20 parts by weight, preferably 0.1 to 10 parts by weight, still more preferably 0.5 to 5 parts by weight based on 100 parts by weight of the water-based ink from the viewpoints of water resistance, rubbing resistance, high-lighter fastness, jetting property and bleeding resistance.

[0079]

As the process for obtaining a water-based ink comprising an aqueous dispersion of polymer particles of pigment-containing water-insoluble polymer having an ionic group at its end (hereinafter referred to as "aqueous dispersion of end ionic polymer"), a process comprising dissolving the water-insoluble polymer in an organic solvent; adding a pigment, water and a neutralizing agent, and a surfactant as occasion demands to the resulting solution; kneading the mixture to form a paste; diluting the paste with water as occasion demands; and distilling off the organic solvent to make it into a water-based system, is preferable.

[0080]

The amount of the colorant in the polymer particles of the water-insoluble polymer is preferably 20 to 1000 parts by weight, more preferably 40 to 800 parts by weight, still more preferably 60 to 600 parts by weight based on the solid content of the water-insoluble polymer from the viewpoints of increasing optical density, facilitating the incorporation of the colorant into the polymer particles and improving water resistance, rubbing resistance and high-lighter fastness.

[0081]

The average particle diameter of the polymer particles of water-insoluble polymer is determined in accordance with the method described in the following Preparation Examples. It is preferable that the average particle diameter is 10 to 500 nm from the viewpoint of dispersion stability.

[0082]

The content of the colorant in the ink is not limited to specified ones as long as satisfactory optical density can be obtained. Usually, the content of the colorant in the ink is preferably 1 to 30% by weight, more preferably 2 to 10% by weight, still more preferably 4 to 8% by weight from the viewpoint of giving satisfactory jetting stability and optical density.

[0083]

There can be added various additives, for instance, a wetting agent such as polyhydric alcohols, a dispersant, a defoaming agent, a mildewproof agent, a chelating agent, a pH adjusting agent and the like to the water-based ink of the present invention.

[0084]

[Examples]

Preparation Examples 1 to 4 (Preparation of Polymer Solutions)

A reaction vessel was charged with monomers, a solvent and a chain transfer agent having an ionic group in the kinds and amounts listed in the column of "Initially Charged Monomers" of Table 1, and nitrogen gas substitution was sufficiently carried out. Thereafter, the temperature was raised to 75°C.

[0085]

On the other hand, a dropping funnel was charged with monomers, a solvent, a chain transfer agent and 2,2'-azobis(2,4-dimethylvaleronitrile) listed in the column of "Dropping Monomers" of Table 1, and the mixture in the reaction vessel was polymerized while adding dropwise the mixture in the dropping funnel to the reaction vessel over a period of 5 hours. Thereafter, the resulting mixture was aged for 2 hours, and methyl isobutyl ketone was then added to the mixture in a proper amount, to give a polymer solution, the solid content of which was 50% by weight.

[0086]

The polymers obtained in Preparation Examples 1 to 3 have an ionic group derived from the chain transfer agent at their ends, and the polymer obtained in Preparation Example 4 does not have the ionic group.

[0087]

A part of the resulting polymer solution was dried under reduced pressure at 105°C for 2 hours and isolated by removing the solvent therefrom. The weight-average molecular weight of the polymer was determined by gel permeation chromatography using chloroform containing 1 mmol/L dodecyldimethylamine as a solvent, with polystyrene as a standard substance.

As a result, the resulting polymer had a weight-average molecular weight as shown in Table 1. The fact that the resulting polymer has an ionic group at its end can be confirmed with an apparatus for nuclear magnetic resonance or the like.

[0088]

Each name listed in Table 1 means the followings:

- Styrenic macromer: commercially available from TOAGOSEI CO., LTD. under the trade name of AS-6 (styrene homopolymerized macromer having a polymerizable functional group of methacryloyloxy group at one end, number-average molecular weight: 6000)
- Monomethoxypolyethylene glycol(n=4) methacrylate: commercially available from Shin-Nakamura Chemical Co., Ltd. under the trade name of NK ESTER M-40G

[0089]

[Table 1]

Preparation Example No.	1	2	3	4
<u>Initially Charged Monomers (Parts by Weight)</u>				
Methyl Ethyl Ketone	30	30	30	30
Methacrylic Acid	3	3	3	3
Styrene	12	12	12	12
Styrenic Macromer	3	3	3	3
Monomethoxypolyethylene	3	3	3	3
Glycol(n = 4) Methacrylate				
Hydroxyethyl Methacrylate	3	3	3	3
Thioglycollic Acid	0.15	0	0	0
Mercaptopropionic Acid	0	0.15	0	0
Mercaptosuccinic Acid	0	0	0.15	0
Mercaptoethanol	0	0	0	0.15
<u>Dropping Monomers (Parts by Weight)</u>				
Methyl Ethyl Ketone	70	70	70	70
Methacrylic Acid	7	7	7	7
Styrene	28	28	28	28
Styrenic Macromer	7	7	7	7
Monomethoxypolyethylene	7	7	7	7
Glycol(n = 4) Methacrylate				
Hydroxyethyl Methacrylate	7	7	7	7
Thioglycollic Acid	0.35	0	0	0
Mercaptopropionic Acid	0	0.35	0	0
Mercaptosuccinic Acid	0	0	0.35	0
Mercaptoethanol	0	0	0	0.35
2,2'-Azobis(2,4-Dimethylvaleronitrile)	1	1	1	1
Weight-Average Molecular Weight	19000	16000	22200	21000

[0090]

Preparation Examples 5 to 12 (Preparation of Aqueous Dispersions of Pigment-Containing Water-Insoluble Polymer Particles)

A pigment, methyl ethyl ketone, ion-exchanged water and a neutralizing agent listed in Table 2 were added to 28 parts by weight of the polymer solution obtained in Preparation Examples 1 to 4 (solid content of the polymer: 50% by weight), and the resulting mixture was sufficiently stirred. Thereafter, the mixture was kneaded twenty times using a triple-roll mill (commercially available from NORITAKE CO., LIMITED under the trade name of NR-84A).

[0091]

The resulting paste was added to 250 parts by weight of ion-exchanged water, and the mixture was sufficiently stirred. Thereafter, methyl ethyl ketone and water were distilled off using an evaporator, to give an aqueous dispersion of pigment-containing water-insoluble polymer particles, the solid content of which was 20% by weight. The average particle diameters of the polymer particles of the resulting water-insoluble polymer was obtained in accordance with the following method. The results are shown in Table 2.

[0092]

[Method of Determining Average Particle Diameters]

The average particle diameter was determined by using a particle size distribution analyzer commercially available from Otsuka Denshi K.K. under the trade name of ELS-8000. As the determination conditions, the temperature of 25°C, the angle between the incident beam and a detector of 90°, the total integrated count of 100 counts, a refractive index (1.333) of water as a refractive index of a dispersing solvent were inputted to the particle size distribution

analyzer. As a standard substance, one commercially available from Seradyn under the trade name of Uniform Microparticles (average particle diameter: 204 nm) was used.

[0093]

Each name listed in Table 2 means the followings:

- Carbon black: commercially available from Degussa under the trade name of Color Black FW18
- Cyan pigment: commercially available from DAINIPPON INK & CHEMICALS, INC. under the trade name of Fastogen Blue TGR-SD

[0094]

[Table 2]

Prep. Ex. No.	Polymer Solution	Pigment	Amount of Each Component (Parts by Weight)			Average Particle Diameter (nm)
			Methyl Ethyl Ketone	Ion-Exchanged Water	Neutralizing Agent 5N-Aqueous NaOH	
5	Prep. Ex. 1	Cyan Pigment	30	5	2.2	128
6	Prep. Ex. 1	Carbon Black	30	5	2.2	120
7	Prep. Ex. 2	Cyan Pigment	30	5	2.2	129
8	Prep. Ex. 2	Carbon Black	30	5	2.2	130
9	Prep. Ex. 3	Cyan Pigment	30	5	2.2	131
10	Prep. Ex. 3	Carbon Black	30	5	2.2	128
11	Prep. Ex. 4	Cyan Pigment	30	5	2.2	128
12	Prep. Ex. 4	Carbon Black	30	5	2.2	130

(Note)

- 1) Preparation Example No. listed in the column of "Polymer Solution" means that the polymer obtained in the specified Preparation Example was used.
- 2) "Average Particle Diameter" means an average particle diameter of the polymer particles.

[0095]

Examples 1 to 6

There were mixed together 20 parts by weight of each of the aqueous dispersions of pigment-containing water-insoluble polymer particles obtained in Preparation Examples 5 to 10, 8 parts by weight of glycerol, 5 parts by weight of polyethylene glycol (molecular weight: 800), 0.2 parts by weight of acetylene glycol-polyethylene oxide adduct (commercially available from Kawaken Fine Chemicals Co., Ltd. under the trade name of Acetylenol EH) and 66.8 parts by weight of ion-exchanged water. The resulting liquid mixture was filtered with a membrane filter (commercially available from Fuji Photo Film Co., Ltd., under the trade name of Disc Capsule CALC120 2.5CMD 50) having a pore diameter of 1.2 µm, to give water-based inks of Examples 1 to 6. Each of these water-based inks contains a water-insoluble polymer having an ionic group at its end.

[0096]

Comparative Examples 1 and 2

The same procedures as in Example 1 were carried out except that in Example 1 the aqueous dispersion of pigment-containing water-insoluble polymer particles was changed to each of the aqueous dispersion of pigment-containing water-insoluble polymer particles obtained in Preparation Examples 11 and 12, to give water-based inks of Comparative Examples 1 and 2. Each of these water-based inks does not contain a water-insoluble polymer having an ionic group at its end.

[0097]

Next, the physical properties of the water-based inks obtained in each of

Examples and Comparative Examples were evaluated in accordance with the methods described below. The results are shown in Table 3.

[0098]

(1) Jetting Property

Continuous printing was carried out on 10 sheets of Canon PB paper at 2000 characters per sheet by using a bubble jet printer (registered trademark) commercially available from CANON INC. under the product number of "F870". Thereafter, a test document including characters, solid images and ruled lines was printed on the paper, and the jetting property was evaluated on the basis of the following evaluation criteria:

[0099]

[Evaluation Criteria]

◎: Satisfactory in all of three items of sharp and clear characters, uniform solid images and no crookedness of printed ruled lines (no problem in actual use)

○: Almost satisfactory in three items of sharp and clear characters, uniform solid images and no crookedness of printed ruled lines (no problem in actual use)

✗: Unsatisfactory in at least one of three items of sharp and clear characters, uniform solid images and no crookedness of printed ruled lines (problem in actual use)

[0100]

(2) Water Resistance

Solid image printing was carried out by using the printer and the paper mentioned above, and the paper was allowed to stand in the air at 25°C for 1 hour. Thereafter, the printed copy paper was immersed vertically in stand-still water for 10 seconds, and the paper was vertically lifted therefrom.

After drying the paper in the air at 25°C, the optical density was determined. The residual ratio of the optical density after immersion to the optical density immediately after solid image printing was obtained. The water resistance was evaluated on the basis of the following evaluation criteria:

[0101]

[Evaluation Criteria]

- ◎: Residual ratio being at least 95%
- : Residual ratio being at least 90% and less than 95%
- △: Residual ratio being at least 70% and less than 90%
- ×: Residual ratio being less than 70%.

[0102]

(3) High Lighter-Fastness

Text printing was carried out by using the printer and the paper mentioned above. After 6 hours passed, the extent of staining of the printed sample when traced with a commercially available aqueous fluorescent marker (commercially available from PILOT CORPORATION, under the trade name of "Spotliter V" OA SGV-15SL) was observed with naked eyes, and the high lighter-fastness was evaluated on the basis of the following evaluation criteria:

[0103]

[Evaluation Criteria]

- ◎: No staining such as rubbed stains was observed even when traced with a fluorescent marker.
- : Some rubbed stains which would cause no problem in practical use were generated when traced with a fluorescent marker.
- ×: Generation of rubbed stains were observed when traced with a

fluorescent marker, which was intolerable.

[0104]

(4) Rubbing Resistance

Solid image printing was carried out on a gloss paper (commercially available from SEIKO EPSON CORPORATION under the trade name of MC gloss paper) by using the above-mentioned printer. After 6 hours passed, the printed surface was strongly rubbed with a finger. The extent of rub-off of the printed image was evaluated on the basis of the following evaluation criteria:

[0105]

[Evaluation Criteria]

◎: Substantially no printed image being rubbed off, and its periphery being not stained.

○: Some printed images being rubbed off, and its periphery being stained a little which would cause no problem in actual use.

✗: Printed images being considerably rubbed off, its periphery being drastically blacked, and finger also being considerably stained.

[0106]

[Table 3]

Ex. No.	Aqueous Dispersion	Jetting Property	Water Resistance	High Lighter-Fastness	Rubbing Resistance
1	Prep. Ex. 5	◎	◎	◎	○
2	Prep. Ex. 6	◎	○	○	○
3	Prep. Ex. 7	◎	◎	◎	○
4	Prep. Ex. 8	◎	◎	◎	○
5	Prep. Ex. 9	◎	○	○	○
6	Prep. Ex. 10	◎	◎	◎	○
Comp. Ex. 1	Prep. Ex. 11	×	△	△	×
Comp. Ex. 2	Prep. Ex. 12	×	△	△	×

(Note)

Preparation Example No. listed in the column of "Aqueous Dispersion" means that the aqueous dispersion obtained in the Preparation Example was used.

[0107]

It can be seen from the results shown in Table 3 that since the water-based inks obtained in Examples 1 to 6 having the polymer having an ionic group at its end is used, the water-based inks are excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property when printed with an inkjet printer.

[0108]

[Effects of the Invention]

The water-based ink of the present invention exhibits some effects such that the water-based ink is excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property when printed with an

inkjet printer.

[Document] Abstract

[Abstract]

[Problems]

To provide a water-based ink which is excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property and blotting resistance when printed with an inkjet printer.

[Solving Means]

A water-based ink containing a colorant and a water-insoluble polymer having an ionic group at its end.

[Selected Drawings] None

BACKGROUND INFORMATION OF APPLICANT

Identification Number	[000000918]
1. Date of Conversion	August 24, 1990
[Reason for Conversion]	New Registration
Address	14-10, 1-chome, Kayaba-cho, Nihonbashi, Chuo-ku, Tokyo
Name	Kao Corporation